

Title	Molecular Characterization of Tri-block Copolymer Containing Polyamino Acid as One Component (Special Issue on Polymer Chemistry, Including Organic Chemistry, XV)
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Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1980), 58(4): 449-456
Issue Date	1980-09-30
URL	http://hdl.handle.net/2433/76908
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Molecular Characterization of Tri-block Copolymer Containing Polyamino Acid as One Component

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Received June 6, 1980

A-B-A type tri-block copolymers (GBG) composed of γ -benzyl-L-glutamate as the A component and butadiene as the B component were prepared. The method of synthesis consists of the polymerization of the γ -benzyl-L-glutamate anhydride initiated by the amine groups capped at both ends of the polybutadiene block which has a moderate degree of polymerization. When dissolved in a helicogenic solvent, such as *N,N'*-dimethylformamide (DMF), the GBG is expected to take a conformation which may be pictured as two rigid rods linked by a flexible joint, since the polybutadiene block portion is intolerant of intrachain hydrogen bonding. Hence, these GBG samples would be considered as a macromolecular model of a once-broken rod with equal rod sections, if the molecular weight of the polypeptide portion was relatively much higher than that of polybutadiene portion. After molecular characterization on these block copolymers by the optical rotatory dispersion measurement was performed, their viscosity behavior in DMF was determined, and the result was compared with the corresponding data on triethylamine (TEA)-initiated PBLG, which assumes the form of a straight rod in DMF. It was found that the values of $[\eta]$ of GBG-block copolymers were 5/8 of those of PBLG homopolymer of equal molecular weight. This finding is in good agreement with the theoretical prediction by Taki-Fujita and Hassager.

KEY WORDS: Tri-block copolymer/ Poly- γ -benzyl-L-glutamate/ Polybutadiene/ A once-broken rod/ α -helix conformation/

INTRODUCTION

In preceding papers,¹⁻³⁾ we have synthesized A-B-A type tri-block copolymers composed of polypeptide blocks and a polydiene block, *i.e.*, A-B-A copolymers composed of poly(γ -benzyl-L-glutamate) (PBLG) (A) and polybutadiene (PB) (B). When this block copolymer is dissolved in a suitable helicogenic solvent, each of the polypeptide portions forms α -helix, *i.e.*, rod-like conformation, while the middle block portion (PB) is intolerant of helix formation and so acts as a flexible joint portion of the polypeptide rods. Such a conformation of the molecule may be pictured as a once-broken rod. According to the theoretical calculation by Yu and Stockmayer,⁴⁾ the intrinsic viscosity $[\eta]$ of a polymer chain composed of two rod sections of equal length connected by a flexible joint, at the limit of infinite length, approaches a value about 15% smaller than that of a straight rod of the same length and diameter, whereas, Taki and Fujita,⁵⁾ and Hassager⁶⁾ have reported, independently, that the value of $[\eta]$ of the once-broken rod is smaller by a factor of 3/8 than that of the straight rod. In the paper by Taki and Fujita, the intrinsic viscosity of the once-broken rod was calculated by means of the method developed by Yamakawa and

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Fujii.⁷⁾ In spite of the theoretical predictions on the viscosity behavior of the once-broken rod molecules in dilute solution, experimental considerations have been very rare and meager.

In the present study, an A-B-A type tri-block copolymer composed of PBLG block as A component and PB block as B component was synthesized by the same method as described earlier.¹⁾

The samples in this study are different from those of earlier study in that the molecular weight of A block was much higher than that of B block in order to neglect the effect of the volume of B block on the overall quantity of the once-broken rod molecules in dilute solution. After molecular characterization on these block copolymers was finished, their intrinsic viscosities in *N,N'*-dimethylformamide (DMF) were determined. Measurement was also performed on triethylamine (TEA)-initiated PBLG homopolymer for comparison.

EXPERIMENTAL

Materials

A di-amine capped polybutadiene (kindly supplied by Drs. K. Rieu and R. Drake of the B. F. Goodrich Chem. Co.) having a number-average molecular weight of 3600 was used as the middle block. The A-B-A tri-block copolymers were prepared by reacting the middle block with *N*-carboxy anhydride of γ -benzyl-L-glutamate in the absence of moisture at room temperature in a dioxane-methylene dichloride mixture. The details of preparation and fractionation of polymer samples were already mentioned in the preceding paper.¹⁾

Measurements

Viscosity measurements were made at 25°C in DMF with an Ubbelohde type viscometer.

To certify the molecular weight heterogeneity of samples, a Water High-Speed GPC Model ALC/GPC 202/R401 (Water Associates, Milford, Mass.) was employed. Four Columns (each 7 mm inner diameter and 30 cm length) of microstyrogel R of 10⁶, 10⁵, 10⁴, and 10³ Å normal pore sizes were used. The carrier solvent used was DMF. The GPC unit was calibrated for the band-broadening effect determining the relation of the V_e , the peak elution volume, with M_e , the molecular weight corresponding elution standard, by using several PBLG homopolymer fractions and a polystyrene standard sample (AMCO).

The molecular weights of the samples were determined from equilibrium runs on DMF solutions of the polymers in a MOM TYPE-3170 ultracentrifuge. In general, solutions of 0.1 to 0.4% (w/v) concentration were used in sedimentation equilibrium runs. The weight-average molecular weight, M_w , of the polymer sample in the cell is given by equation 1

$$M_w = \frac{2RT}{\omega^2(1-\bar{v}_p)} \cdot \frac{c_b - c_m}{c_0} \cdot \frac{1}{r_b^2 - r_m^2} \quad (1)$$

where, R is the universal gas constant, T is the absolute temperature, ω is the angular velocity of the rotar, \bar{v} is the partial specific volume of the solute, ρ is the density of the solution (assumed equal to the density of DMF), c_b and c_m are concentrations at r_b and r_m , respectively, *i.e.*, at the bottom of the cell and at the meniscus, and c_0 is the uniform concentration before centrifugation. The molecular weights of PBLG homopolymers and GBG block copolymers were found to be almost independent of concentration over the

range of 0.1 to 0.4%.

Optical rotatory dispersion (ORD) measurements were carried out with a Yanagimoto OR-100 Type spectropolarimeter using a tungsten lamp as light source in a temperature range from 10° to 40°C. The wave-lengths used ranged from 325 to 570 nm. The concentration of polymer solution was 1.0 g/dl throughout these measurements. The reduced mean residue rotation, $[m']_i$ (deg cm²/dmol), was calculated from the observed rotation, α_i , at each wave-length using the equation 3

$$[m']_i = [3/(n^2 + 2)](100/cL)\alpha_i \quad (2)$$

where n is the refractive index of the solution, c is the concentration in moles of residues/liter, and L is the cell path length in centimeter. The parameters a_0 and b_0 of the Moffitt-Yang equation⁸) were obtained as suggested by Urnes and Doty.⁹⁾ The quantity $[m']_i(\lambda^2 - \lambda_0^2)/\lambda_0^2$ was plotted against $\lambda_0^2/(\lambda^2 - \lambda_0^2)$, using $\lambda_0 = 212$ nm; a_0 and b_0 were obtained as the intercept and the slope, respectively, of the resulting straight line.

RESULTS AND DISCUSSION

A. Synthesis and Characterization

The composition, molecular weight and $[\eta]$ in DMF at 25°C of the polymer samples are shown in Table I. Polydispersity of block copolymers was examined by GPC. Figure 1 illustrates the GPC diagram showing corrected UV chromatograms (the amount of the detector response) plotted against elution count V_e for the GBG-88 sample together with the result on a polystyrene standard sample ($M_w = 1.1 \times 10^5$, $M_w/M_n = 1.06$), in DMF solution. The experimental chromatogram for the GBG-88 sample shows a very small tailing of the main component and a single, rather sharp peak similar to that of the standard polystyrene. This may mean that the GBG copolymer is sufficiently homologous with respect to both molecular weight and composition.

B. Helix-Coil Transition Temperature

Table I. Molecular Characterization of Samples

Sample Code	Butadiene (mol-%)	$[\eta]$ (dl/g) (DMF, 25°C)	M_w	T_t (°C)	$\Delta H_{\theta H}$ (Kcal/mol)
GBG-97	3.0	6.4	480,000	27.0	77
GBG-96	3.5	4.5	470,000	27.9	75
GBG-96-2	4.0			28.4	73
GBG-95	5.0	3.4	310,000	28.8	71
GBG-88	12.0				
PBLG-1		12.8	588,000	26.0	80
PBLG-2		7.4	370,400	26.5	80
PBLG-3		2.8	197,000	28.0	76
PBLG-4		1.0	98,000	30.6	65
PBLG-5		0.70	77,000		
PBLG-5		0.36	47,900		

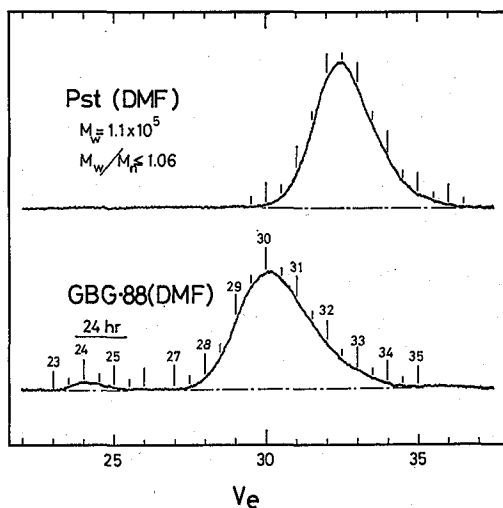


Fig. 1. Molecular weight heterogeneity for GBG-88 block copolymer as estimated by GPC in DMF solution.

The thermally induced conformational transition of GBG and PBLG from the coil conformation at low temperatures to the helix conformation at high temperatures was studied in DCA(76)-DCE(24) (v/v) mixture by ORD. Figures 2 and 3 illustrate the experimental results obtained for PBLG and GBG copolymers, respectively, showing the change of b_0 with temperature. The transition was found to be completely reversible for both cases. The transition temperature T_t of PBLG and GBG increases with decreasing molecular weight of G-component. While, the value of van't Hoff heat of transition, $\Delta H_{\theta H}$ is readily determined experimentally from the slope of the b_0 against temperature plot using the equation.¹⁰⁾

$$\left(\frac{df_H}{dT}\right)_{T_t} = \frac{1}{b_{0,h} - b_{0,c}} \left(\frac{db_0}{dT}\right)_{T_t} = \frac{\Delta H_{\theta H}}{4RT_t^2} \quad (3)$$

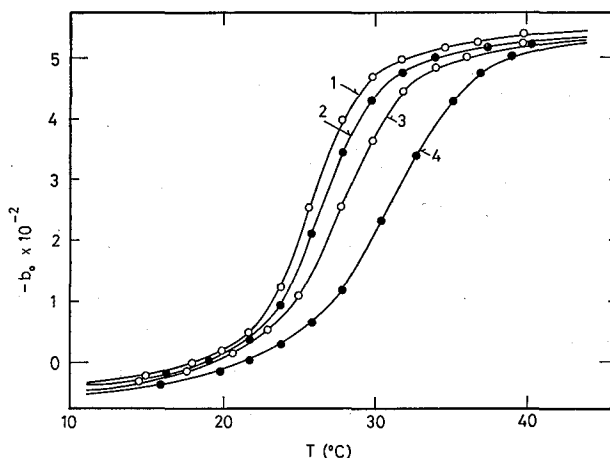


Fig. 2. Temperature dependence of Moffitt-Yang parameter b_0 of PBLG in DCA(76)-DCE(24) (v/v) mixture. (1) PBLG-1 ($M=588,000$), (2) PBLG-2 ($M=370,400$), (3) PBLG-3 ($M=197,000$), and (4) PBLG-4 ($M=98,000$).

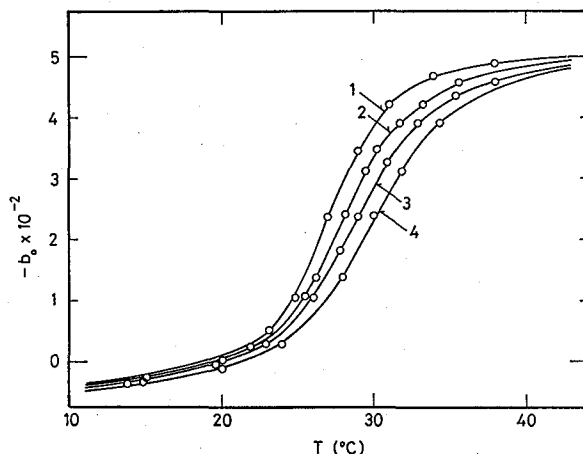


Fig. 3. Temperature dependence of Moffitt-Yang parameter b_0 of GBG block copolymer in DCA(76)-DCE(24) (v/v) mixture. (1) GBG-97 ($M=480,000$), (2) GBG-96 ($M=470,000$), (3) GBG-96-2, and (4) GBG-95 ($M=310,000$).

where $b_{0,h}$ and $b_{0,c}$ are the values of b_0 for the complete helix and complete coil, respectively. $b_{0,h}$ was assigned -630 from ORD measurements in DCE at 25°C ,¹¹⁾ while $b_{0,c}$ was assigned 0 from ones in DCA at 25°C ,¹¹⁾ both for PBLG. The $\Delta H_{\alpha H}$ and T_t obtained are listed in Table I. It should be pointed out that the $\Delta H_{\alpha H}$ values decrease with decreasing molecular weight.

According to the statistical mechanical theory of Lifson and Roig for the helix-coil transition of polypeptide,¹²⁾ if its molecular weight M is sufficiently large, the helix content f_H can be expressed by

$$f_H = f_H^\infty (1 - K/M) \quad (4)$$

where f_H^∞ is the helix content for the infinitely long chain. In this equation, f_H^∞ and K are the constants dependent only on temperature for a given polypeptide-solvent system. Teramoto *et al.*¹³⁾ derived an asymptotic series equation which expresses the helix-coil transition temperature T_t (for $f_H=1/2$) for the polypeptide whose molecular weight is M as a function of the molecular weight

$$T_t = T_t^\infty + K'/M + O(1/M^2) \quad (5)$$

where T_t^∞ is the values of T_t for infinite molecular weight and K' is a constant independent of M . For the second step, it may be a simple matter to extend the above treatments to the case where the polypeptide molecule contains one intrachain defect which cannot participate in the formation of helix. If such a defect appears at the mid-point of the chain molecule, and if the defect acts in the same way as the chain end of the molecule does in the formation of helix, then the equation 6 will be derived by assuming that there exists no thermodynamic interaction between the two polypeptide chains extending on

$$T_t = T_t^\infty + 2K'/M + O(1/M^2) \quad (6)$$

both sides of the intrachain defect and hence they may be regarded as independent molecules.

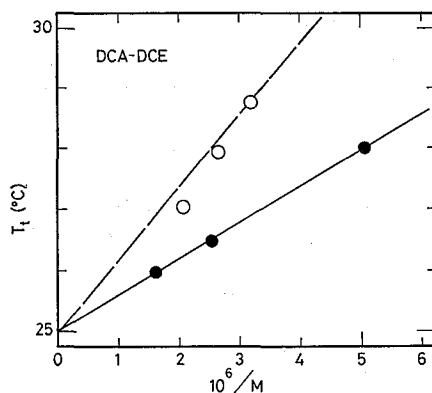


Fig. 4. Helix-Coil transition temperature T_t in a DCA(76)–DCE(24) (v/v) mixture as a function of $1/M$; for PBLG (●) and for GBG block copolymer (O).

In Figure 4, the values of T_t for PBLG are plotted against $1/M$. It can be seen that the experimental points fall approximately on a straight line, in agreement with the theoretical prediction shown above. Next, the values of T_t obtained on GBG copolymers as a function of $1/M$ are also shown in Figure 4, and here the points also fall on a straight line in the range of molecular weights investigated here. Furthermore, the slope of the line for GBG is just 2 times as large as that for PBLG. Thus, it may be concluded that the GBG block copolymer obeys a model in which the two rod-like sections of G-block chains are of equal length and the intervening short flexible section of the PB block is represented by a universal joint connecting the two rods, as illustrated in Figure 5.

C. Intrinsic Viscosity of Once-Broken Rod

Taki and Fujita⁵⁾ obtained an equation which described the intrinsic viscosity $[\eta]_b$ of a once-broken rod with equal rod sections connected by a completely flexible joint

$$[\eta]_b = \frac{5NaL^3}{192M} \cdot \frac{1}{\ln(L/d) + \ln 2 - 11/6} \quad (7)$$

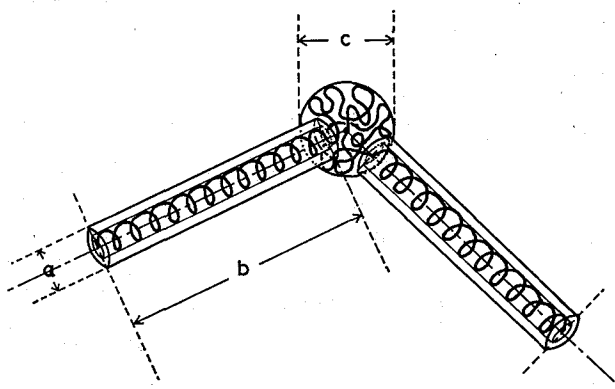


Fig. 5. A schematic model for the molecular conformation of the A–B–A type block copolymer consisting of α -helical PBLG as the A component and polybutadiene as the B component.

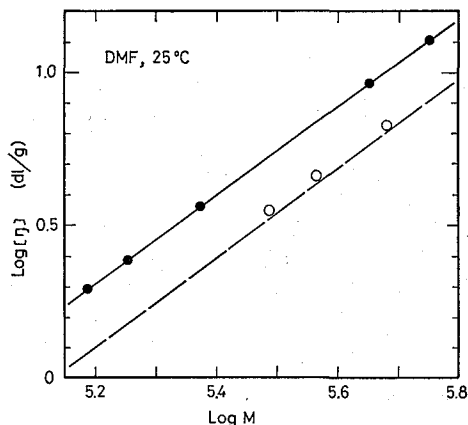


Fig. 6. The intrinsic viscosity $[\eta]$ of PBLG (●) and GBG block copolymer (○) in DMF at 25°C as a function of molecular weight.

where N_a is the Avogadro number, M is the molecular weight, L is the length of the rods, and d is the diameter of the rod. The constant $\ln 2 - 11/6$ in equation 7 actually represents the leading correction for hydrodynamic interactions between the two rod sections.

Until that time, Yamakawa and Fujii⁷⁾ had already derived an equation for the intrinsic viscosity $[\eta]_s$ of a straight rod as

$$[\eta]_s = \frac{N_a L^3}{24 M} \cdot \frac{1}{\ln(L/d) + 2 \ln 2 - (7/3)} \quad (8)$$

Thus, the numerical value of the ratio of the intrinsic viscosity for the once-broken rod to that for the straight rod, $[\eta]_b/[\eta]_s$, becomes 5/8 at the limit of infinite L/d . Hassager⁶⁾ has also reported the value 5/8 as the asymptotic value of the ratio of $[\eta]_b$ to $[\eta]_s$ using a different method of analysis.

Figure 6 illustrates plots of the intrinsic viscosity versus M in logarithmic scale for GBG block copolymers and PBLG homopolymers in DMF at 25°C. It is shown that the data for GBG fall on the straight line (dashed line) calculated from the solid line for PBLG by assuming $[\eta]_b/[\eta]_s$ is 5/8, with a little deviation.

In conclusion, it was found that the values of the intrinsic viscosity for rather high molecular weight GBG block copolymers in DMF were 5/8 of the corresponding values for PBLG homopolymer of equal molecular weight as clearly shown in Figure 6, that is, our experimental result is in excellent agreement with the theoretical value predicted by Taki-Fujita and Hassager.

ACKNOWLEDGMENT

The authors acknowledge Dr. H. Suzuki in the Institute for Chemical Research, Kyoto University for his help with the GPC measurement. They also wish to thank Dr. M. Oka in the Department of Polymer Chemistry, Kyoto University for his helpful advices. This work was supported by the Grant-in-aid from the Ministry of Education, to which acknowledgment is made.

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